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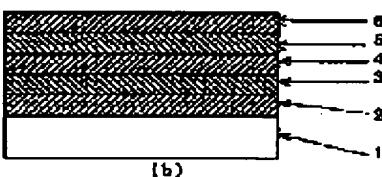
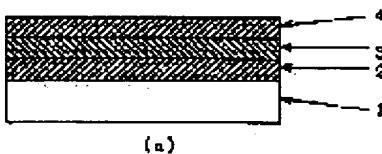
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(54) TRANSPARENT CONDUCTIVE FILM AND FORMATION OF TRANSPARENT ELECTRODE

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance not only low specific resistance and durability but also minuscule electrode processability by adding ZnO to a transparent oxide layer to obtain an oxide layer containing In within a specific value range with respect to the sum total of Zn and In and forming a metal layer as an Ag-containing metal layer.

SOLUTION: As a substrate 1, a glass plate, a resin film or the like is used. Transparent oxide layers 2, 4, 6 are oxide layers containing ZnO and containing In within a 9-98 atomic % range with respect to the sum total of Zn and In and enhanced in the durability against an alkali soln. or an acidic soln. Subsequently, since metal layers 3, 5 contain Ag and the transparent oxide layers contain ZnO, the crystallization of Ag is accelerated even under a low temp. film forming condition of 150° C or lower and the lowering of the specific resistance of the Ag-containing metal layers and the reduction of the flocculation of Ag are prevented. By this constitution, low specific resistance can be easily realized and durability such as alkali resistance, humidity resistance or the like can be enhanced.



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CLAIMS

[Claim(s)]

[Claim 1] It is the transparent electric conduction film which a transparent oxide layer is an oxide layer which contains In in the range of 9 – 98 atom % to total with Zn and In, including ZnO in the transparent electric conduction film with which it comes to carry out the layer (2n+1) (for n to be one or more integers) laminating of a transparent oxide layer and the metal layer to this order, and is characterized by a metal layer being a metal layer containing Ag from a base side.

[Claim 2] At least one layer of a transparent oxide layer is In₂O₃. Transparent electric conduction film according to claim 1 which is the layer which consists of a multilayer of the film made into a principal component, and the film which makes ZnO a principal component.

[Claim 3] The transparent oxide layer which is most separated from a base is In₂O₃. Transparent electric conduction film according to claim 1 or 2 which is the layer which consists of a multilayer of the film made into a principal component, and the film which makes ZnO a principal component, and is the layer which consists of a multilayer on which the film which tends to keep away from a base put the film so that the content of In might increase.

[Claim 4] The transparent oxide layer near a base is In₂O₃. Transparent electric conduction film according to claim 1 or 2 which is the layer which consists of a multilayer of the film made into a principal component, and the film which makes ZnO a principal component, and is the layer which consists of a multilayer on which the film which tends to approach a base put the film so that the content of In might increase.

[Claim 5] At least one layer of a transparent oxide layer is In₂O₃. Transparent electric conduction film according to claim 1 which is a layer containing a mixed oxide with ZnO.

[Claim 6] The transparent oxide layer which is most separated from a base is In₂O₃. Transparent electric conduction film according to claim 1 or 5 which is a layer containing a mixed oxide with ZnO, and is the layer which has the inclination composition which In content increases in the direction of thickness as it goes in the direction which keeps away from a base.

[Claim 7] The transparent oxide layer near a base is In₂O₃. Transparent electric conduction film according to claim 1 or 5 which is a layer containing a mixed oxide with ZnO, and is the layer which has the inclination composition which In content increases in the direction of thickness as it goes in the direction approaching a base.

[Claim 8] At least one layer of a transparent oxide layer is In₂O₃. The layer containing a mixed oxide with ZnO, Or In₂O₃ In the portion which touches the metal layer in which it is the layer which consists of a multilayer of the film made into a principal component, and the film which makes ZnO a principal component, and the transparent oxide layer concerned contains Ag. The transparent electric conduction film of the claim 1-7 which is the oxide layer which contains Zn more than 50 atom % to total with Zn and In given in any 1 term.

[Claim 9] At least one layer of a transparent oxide layer is In₂O₃. Transparent electric conduction film of a claim 1-8 given in any 1 term with which the film which is the layer which consists of a multilayer of the film made into a principal component and the film which makes ZnO a principal component, and makes ZnO a principal component contains Ga.

[Claim 10] The transparent electric conduction film of the claim 1-9 which is the layer which at least one-layer metal layer turns into from the alloy film of Ag and other metals given in any 1 term.

[Claim 11] The transparent electric conduction film of the claim 1-9 which is the layer which consists of a multilayer with the metal layer which at least one-layer metal layer turns into from the metal layer containing Ag, and other metals given in any 1 term.

[Claim 12] The transparent electric conduction film of the claim 1-9 which is the layer which has the inclination composition from which at least one-layer metal layer consists of Ag and other metals, and Ag concentration changes in the direction of layer thickness given in any 1 term.

[Claim 13] The transparent electric conduction film according to claim 10, 11, or 12 other metals of whose are Au and/or Pd.

[Claim 14] The formation method of the transparent electrode which carries out patterning when hydrogen ion concentration *****s using the acid solution which is 0.01-9M, after forming the transparent electric conduction film of a claim 1-13 given in any 1 term on a base.

[Claim 15] The formation method of a transparent electrode according to claim 14 using the acid solution by which the oxidizer which has the oxidation to Ag as acid solution was added.

[Claim 16] The substrate with electrode wiring for liquid crystal displays in which the source electrode, drain electrode, and pixel electrode of a TFT type liquid crystal display were formed by the transparent electric conduction film of a claim 1-13 given in any 1 term.

[Claim 17] The formation method of the substrate with electrode wiring for liquid crystal displays characterized by forming the transparent electric conduction film of a claim 1-13 given in any 1 term, and forming the drain electrode which subsequently united this transparent electric conduction film with the source electrode and the pixel electrode by carrying out etching processing after forming a gate electrode, a gate insulator layer, and a semiconductor layer on a base.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the transparent electric conduction film used for a liquid crystal display (LCD) etc., and the formation method of a transparent electrode.

[0002]

[Description of the Prior Art] Now, the mixed-oxide (henceforth InSnx Oy) film of In and Sn is widely used as an electrode for LCD. Especially, in the STN type color LCD, with the highly-minute-izing and big-screen-izing, the line breadth of the transparent electrode for a liquid crystal drive is also thinner, and the thing of a long configuration is needed. For this reason, the transparent electric conduction film of very low resistance below 3ohms of sheet resistance and ** is needed. In order to attain this sheet resistance, it is necessary to achieve thick-film-izing (300nm or more) of a transparent electric conduction film, or low specific resistance-ization (below 100micro ohm-cm).

[0003] However, since problems, like the level difference by the existence of that the membrane formation cost of 1 transparent electric conduction film increases, that the difficulty of 2 electrode patterning increases, and three transparent electrodes becomes large, and orientation control of liquid crystal becomes difficult arise, thick-film-ization has a limitation. On the other hand, it is InSnx Oy. Although how to form the film itself into low specific resistance is also examined, it is the low resistance InSnx Oy below 100micro ohm-cm. The method of being stabilized and producing a film is not established yet.

[0004] On the other hand, as a method of obtaining easily the low resistance transparent electric conduction film below 100micro ohm-cm, it is InSnx Oy about Ag layer. InSnx Oy/Ag/InSnx Oy inserted in the layer The composition to say is known. However, although this composition is also low specific resistance, endurance is so inadequate that the white fault considered to be film ablation by indoor neglect is produced. Moreover, the processability — also in the case of electrode processing by etching using acid solution, side etching advances and ablation is looked at by the pattern edge section — is insufficient.

[0005] For this reason, InSnx Oy/Ag/InSnx Oy The substrate of composition is not put in practical use as a transparent electric conduction substrate for LCD until now, while low resistance has the advantage acquired easily.

[0006]

[Problem(s) to be Solved by the Invention] this invention aims at offer of the transparent electric conduction film which is used for LCD etc. and which is low specific resistance, was excellent in endurance, and was excellent in detailed electrode processability ability, and the formation method of a transparent electrode.

[0007]

[Means for Solving the Problem] In the transparent electric conduction film with which, as for this invention, it comes to carry out the layer (2n+1) (for n to be one or more integers) laminating of a transparent oxide layer and the metal layer to this order on a base from a base side a transparent oxide layer Including ZnO, it is the oxide layer which contains In in the range of 9 - 98 atom % to total with Zn and In, and the transparent electric conduction film characterized by a metal layer being a metal layer containing Ag is offered.

[0008] In the case of n= 1, the cross section of the transparent electric conduction film of this invention in n= 2 is shown in drawing 1 (a) at drawing 1 (b). 1 is a metal layer in which a base, and 2, 4 and 6 contain three and a transparent oxide layer and 5 contain Ag. The transparent oxide layers 2, 4, and 6 are oxide layers which contain In in the range of 9 - 98 atom % to total with Zn and In, including ZnO. Especially the content rate of In has desirable 45 - 95 atom %.

[0009] Since a transparent oxide layer contains ZnO, this invention is conventional InSnx Oy. As compared with the case where a film is used, it also sets under a low-temperature membrane formation condition 150 degrees C or less. It not only prevents the reduction in resistance of a metal layer (henceforth Ag layer) and the isoagglutination of Ag which stimulate crystallization of Ag and contain Ag, but The adhesion force of the interface of the oxide layer and Ag layer containing ZnO improves, consequently moisture resistance and the processability (henceforth patterning nature) of the detailed electrode pattern by acid solution improve remarkably.

[0010] under the present circumstances, Ag layer and a ZnO component — wealth — constituting so that a layer may touch is desirable In the oxide layer which touches Ag layer especially, it is desirable to contain Zn more than 50 atom % to total with Zn and In in the portion which touches Ag layer. In this case, the portion to which Zn touches 100 atom %, i.e., Ag layer, may serve as ZnO which does not contain In. As for especially the thickness of the portion which touches Ag layer, it is desirable to be referred to as 5nm or more 1nm or more.

[0011] Moreover, since an oxide layer contains In in the range of 9 - 98 atom % to total with Zn and In, in addition to the outstanding feature which the above-mentioned ZnO has, the endurance over an alkali solution or an acidic solution improves.

[0012] As a base 1 in this invention, a glass plate, the film made of a resin, etc. are used. Moreover, a base as shown in drawing 2 is also used. The substrate for colors LCD which is equivalent to the base 1 of drawing 1 at drawing 2 is shown. As for the light-filter layer from which 39 becomes a glass substrate and 7 becomes a color pixel, and 8, a transparent resin protective layer and 9 are non-in-a-plane intermediate layers. The transparent resin protective layer 8 protects and smooths a light-filter layer. the thing for the non-in-a-plane intermediate layer 9 raising the adhesion of the transparent resin protective layer 8 and a transparent electric conduction film — it is — a silica and SiNx etc. — it is used

[0013] At least one layer of a transparent oxide layer is 1In 2O3. As shown in the layer which consists of a mixed oxide with ZnO, or 2 drawing 3 . it is In 2O3. It is the layer which consists of a multilayer of the film 10 made into a principal component, and the film 11 which makes ZnO a principal component. As for all transparent oxide layers, it is desirable to be unified by the type of

either 1 or 2 practical.

[0014] The total thickness of the transparent oxide layer 2 is [as opposed to / the total thickness / when a transparent oxide layer is a layer which consists of a multilayer] In 2O3 at 10–200nm. It is desirable that the thickness ratio of the sum total of a film 10 made into a principal component is 5 – 95%. The same is said of the transparent oxide layers 4 and 6. Alkali resistance improves by considering as such composition, without spoiling moisture resistance and patterning nature. Especially, it is desirable that it is 45 – 95%. In addition, in this specification, "thickness" means geometric thickness.

[0015] In 2O3 as shown in a drawing 4 (a) as a transparent oxide layer 6 which is most separated from a base It is the layer which consists of a multilayer of the film made into a principal component, and the film which makes ZnO a principal component. It considers as the layer which consists of a multilayer on which the film which tends to keep away from a base put the film so that the content (In to total with Zn and In comparatively) of In might increase, Or In 2O3 as shown in b drawing 4 (b) It is a mixed-oxide layer with ZnO, and it is desirable to consider as the layer which has the inclination composition which In content increases in the direction of thickness as it goes in the direction which keeps away from a base. In addition, drawing 4 (b) shows signs that the content of In of the transparent oxide layer 6 increases towards keeping away from a substrate.

[0016] For a film with few contents of In than the oxide film 13, and 13, as for the portion of under 50 atom %, and 40, in drawing 4, the content of In is [a film with more contents of In than the oxide film 12, and 14 / the content of 12 of In] a portion more than 50 atom %.

a) Or excel in the corrosion and endurance over an alkali solution or an acidic solution by considering as the composition of b.

[0017] As an example of creation in a), it is the film and In 2O3 which make ZnO a principal component from a base side. In 2O3 to the thickness which carries out the laminating of the film made into a principal component in this order, and makes ZnO a principal component, so that it goes in the direction which keeps away from a base The thickness ratio of the film made into a principal component is made to increase, and it is In 2O3 about the best layer. What is necessary is just to consider as

[0018] It is In 2O3 towards carrying out sputtering of the target which makes ZnO a principal component, and the target which makes In 2O3 a principal component simultaneously as an example of creation in b), and keeping away from a base. It is realizable by changing the sputtering power of each target so that a composition ratio may increase. Moreover, some ZnO(s) and In(s) 2O3 It is In 2O3 towards keeping away the mixed-oxide target with which composition ratios differ from a base. In turn which a composition ratio increases, it is realizable also by carrying out sputtering one by one.

[0019] Moreover, In 2O3 as shown in c drawing 4 (c) as a transparent oxide layer 2 near a base It is the layer which consists of a multilayer of the film made into a principal component, and the film which makes ZnO a principal component. It considers as the layer which consists of a multilayer on which the film which tends to approach a base put the film so that the content of In might increase, Or it is the mixed-oxide layer of In₂O₃ and ZnO as shown in d drawing 4 (d), and it is desirable to consider as the layer which has the inclination composition which In content increases in the direction of thickness as it goes in a base and the direction which approaches. In addition, drawing 4 (d) shows signs that it increases towards the content of In of the transparent oxide layer 2 approaching a substrate. c) Or by considering as the composition of d, the adhesion force when contacting an alkali solution and an acidic solution improves remarkably.

[0020] a) When it considers as the composition of -d, the thickness of this transparent oxide layer has the viewpoint of a color tone and a visible light transmittance to desirable 10–200nm. Moreover, In 2O3 on this film to the thickness of the film which makes ZnO a principal component in the composition of a-d Thickness of the sum total of the thickness ratio of the film made into a principal component of one or more portions (It is a from a substrate side about the best oxide layer 6) the case where it is referred to as ZnO(7nm)/In₂O₃(3nm) cZnO(5nm)/In₂O₃(5nm) eZnO(3nm)/In 2O3 (20nm) — the sum total thickness of c-f — or The thickness of the portion into which In content exceeds 50 atom % has patterning nature and an alkali-proof viewpoint to desirable 5–50nm. It is for alkali resistance not to be excellent in less than 5nm, and for patterning nature to fall in 50nm **.

[0021] It is desirable from a viewpoint of alkali resistance and patterning nature that In content is [the lower layer portions 12 or 14 of the transparent oxide layer 6 which is most separated from a base in the composition of a or b especially] 50 to 90 atom % s, the content of In is [the amount of / 13 or 40 / management] more than 90 atom %, and the thickness for a management 13 or 40 is 5–50nm.

[0022] In this invention, when forming the film which makes ZnO a principal component, as for this film, it is desirable to contain Ga. ZnO which specifically contains Ga is desirable. Although conductivity is shown when trivalent dopants, such as aluminum, are added to ZnO which is an insulator, what added Ga shows the best conductivity and a visible light transmittance.

[0023] Moreover, although Zn metal can also be used as a target when high DC sputtering of mass-production nature is assumed as a method of forming ZnO, there is a difficulty that the margin of membrane formation conditions is narrow. By adding Ga, DC sputtering from a ZnO target becomes possible, and the margin of the membrane formation condition also becomes very large at Zn.

[0024] As for the content rate of Ga, it is desirable that it is one to 15 atom % to total with Zn and Ga. Membrane formation speed becomes slow under by 1% atom, and a visible light transmittance becomes [the amount of dopes] low by 15 atom % **.

[0025] As for one or more layers of the metal layer in this invention, it is desirable to consider as the layer which has the inclination composition from which it consists of a layer of the multilayer composition which consists of the layer and 2Ag layers which consist of an alloy film of 1Ag and other metals, and other metal layers, or 3Ag and other metals, and Ag concentration changes in the direction of layer thickness.

[0026] It is also desirable in the above 2 (for example, other metal layers), to constitute so that it may be placed between an interface with a transparent oxide layer. In this case, although an interface has more than one, it constitutes so that it may be placed between at least one interface.

[0027] The damp-proof fall by the isoagglutination of Ag can be improved by using a metal layer as one alloy layer, 2 multilayer composition layers, or 3 inclination composition film as mentioned above, without spoiling low resistance and high visible high permeability.

[0028] As for each thickness of a metal layer (equivalent to 3 of drawing 5 and drawing 6 , and 5), it is desirable that it is 3–20nm at any [of the above 1–3] case. In less than 3nm, sheet resistance becomes high, and a visible light transmittance falls in 20nm **.

[0029] Since it says that the fall of resistance, improvement in permeability, and improvement in endurance can be satisfied as other metals, one or more sorts of metals chosen from the group which consists of Pd, Au, Cu, Zn, Sn, Ti, Zr, V, nickel, Cr, Pt, Rh, Ir, W, Mo, and aluminum are desirable. Especially, it is desirable that other metals are Au and/or Pd. The isoagglutination of Ag is prevented and high Ag film of endurance is obtained by addition of Au or Pd.

[0030] As other metals, Pd is mentioned as an example and the composition of the metal layer of the above 1-3 is explained concretely. As composition of the above 1, the layer (it is called a PdAg alloy layer) which consists of an alloy film of Ag and Pd is used. In a PdAg alloy layer, Pd exists uniformly in Ag. In this case, as for the content rate of Pd in a PdAg alloy layer, it is desirable that it is 0.1 to 5.0 atom % to total with Ag. Endurance becomes inadequate under by 0.1 atom %, and the decline in a visible light transmittance and the rise of resistance are brought about in 5.0 atom % **.

[0031] As composition of the above 2, as shown in drawing 5 (a), it is placed between the interfaces of the transparent oxide layers 2 and 4 and the Ag layer 16 by the Pd layers (intervention layer) 15 and 17. In this case, the range of the thickness of the intervention layers 15 and 17 has desirable 0.1-3nm. If it intervenes by this thickness, the effect which adds Pd of the above 1, and the same effect will be acquired. Intervention layer thickness becomes insufficient [less than 0.1nm / endurance], and a visible light transmittance falls in 3nm **. Especially, 0.1-1nm is desirable. Moreover, as composition of the above 2, as shown in drawing 6 (a), it is good also as multilayer composition of the Ag layer 22 and the Pd layer 21. In this case, it is desirable to set thickness of 0.1-3nm and each Ag layer 22 to 1-20nm for the thickness of each Pd layer 21.

[0032] As composition of the above 3, as shown in drawing 5 (b) or drawing 6 (b), the layer which has the inclination composition from which Ag concentration changes is used in the direction of layer thickness. In this case, as shown in the composition between which it is placed by the Pd rich layers 18 and 20 to which Pd concentration becomes high, and drawing 6 (b), the multilayer composition of the Ag rich layer 19 and the Pd rich layers 18, 20, 23, and 24 etc. is used.

[0033] In the Pd rich layers 18, 20, 23, and 24, as shown in drawing 5 (b), it is the layer [as / whose Pd is more than 50 atom % to total with Ag and Pd]. Pd rich layer thickness becomes insufficient [0.1nm / endurance], and in 3nm **, since it is in the inclination for a visible light transmittance to fall, the thickness of 0.1-3nm is suitable for it.

[0034] By choosing each layer thickness which constitutes a transparent electric conduction film within the limits of the above-mentioned, adjustment of the permeability by the optical interference effect and a color tone and adjustment of sheet resistance can be performed. As an example of the composition of a transparent electric conduction film of coming to carry out the layer (2n+1) (for n to be one or more integers) laminating of this invention a) A base / transparent oxide layer (5-30nm) / metal layer (5-20nm) / transparent oxide layer (30-50nm), b) — a transparent oxide layer (30-50nm) — there is a /metal layer (5-20nm) / transparent oxide layer (80-120nm) / metal layer (5-20nm) / a transparent oxide layer (30-50nm)

[0035] Although the transparent electric conduction film of this invention shows low sheet resistance, a high visible light transmittance, and high endurance, in order to raise a property further, it may give 100-300-degree C heat-treatment after membrane formation. With this heat treatment, crystallization of an oxide layer and Ag layer and stabilization are urged, lower resistance and a higher visible light transmittance are obtained, and thermal resistance also improves.

[0036] Since the low resistance below 3ohms / ** is obtained easily, the transparent electric conduction film of this invention is the optimal as a transparent-electrode film of the electronic display which makes LCD the start and needs low resistance of an electroluminescence display, a plasma display, or an electrochromic element. Especially, the effect excellent in display upgrade, such as enlargement of a screen product and cross talk reduction, is demonstrated by using the transparent electric conduction film of this invention in simple matrix type LCD.

[0037] After forming the aforementioned transparent electric conduction film on a base, this invention offers the transparent-electrode formation method which carries out patterning again, when hydrogen ion concentration ***** using the acid solution which is 0.01-9M. By using the formation method of the transparent electrode of this invention, it is suitable as a transparent electrode of various transparent electric conduction substrates for a display, such as LCD as which patterning with an amount [of side etching] of 5 micrometers or less becomes possible, and a detailed dimensional accuracy is required.

[0038] After forming a desired resist pattern by the photolithography method on a transparent electric conduction film as shown in drawing 1 as the first patterning method, performing patterning by ***** using the acid solution of hydrogen ion concentration 0.01-9M (mol/l) is mentioned. The density range from which the amount of side etching is set to 5 micrometers or less also in this hydrogen-ion-concentration range is desirable. In the acid solution below hydrogen-ion-concentration 0.01M, by the acid solution of hydrogen-ion-concentration 9M **, etching will hardly progress, but an etch rate becomes quick, controlling will become difficult or the amount of side etching will also advance greatly exceeding 5 micrometers.

[0039] As acid solution, the solution which makes a principal component a hydrochloric acid, a hydrobromic acid, a hydroiodic acid, a nitric acid, a sulfuric acid, and a ferric chloride is mentioned. An etch rate is large especially, and since it says that side etching is small, the acid solution which makes a hydrochloric acid or a hydrobromic acid a principal component is desirable.

[0040] moreover, the acid solution of the above-mentioned [reason / for the ability to etch Ag layer efficiently] — Ag — oxidation reduction potential — ** — it is desirable to add an oxidizer (for it to have an oxidation operation to Ag) The dissolution rate of Ag can be raised by addition of an oxidizer, and better patterning nature is obtained. Moreover, addition of an oxidizer is effective also from the point of dissolving indium oxide efficiently. As an oxidizer, a nitrous acid, a hydrogen peroxide, potassium permanganate, a potassium iodate, the second cerium ammonium of a nitric acid, a ferric chloride, etc. are mentioned. Especially, a ferric chloride is desirable.

[0041] In this case, things are [adding an oxidizer in acid solution, and hydrogen ion concentration being 0.01-9M, and making it oxidizer concentration be 0.0001-1.5M] desirable. Out of this density range, etching of Ag layer stops being able to go on easily, an etch residue arises or the amount of side etching becomes large exceeding 5 micrometers. Or an etch rate becomes quick and it becomes difficult to control it.

[0042] Since it says that the etch rate which is especially easy to control being obtained, and side etching are small, the acid solution which makes a principal component a ferric chloride, a hydrochloric acid, or a ferric chloride and a hydrobromic acid is desirable. Since the amount of side etching specifically says that 2-4 micrometers and very good patterning nature are obtained, it is mentioned as an example with a desirable combination from which a hydrochloric acid is set to 0.1-5M by the ferric chloride with hydrogen ion concentration to 0.01-1.5M and from which it combines or a hydrobromic acid is set to 3-9M by the ferric chloride with hydrogen ion concentration to 0.0005-0.5M.

[0043] a zinc oxide although it is desirable to use the concentration of an acid and an oxidizer, optimizing suitably according to each film composition, as shown in Examples 4, 6, and 19 as an oxide layer — when a rich oxide is used, good patterning only of an acid becomes possible the indium oxide which is hard to dissolve only from an acid on the other hand — when carrying out patterning of the film using the rich oxide, it is desirable to add an oxidizer within the limits of the above [reason / for being easy to dissolve indium oxide]

[0044] In this invention, although it is immersed in the solution of an alkali-halide metal salt, or the solution of a sodium thiosulfate after ***** as acid solution using the acid solution containing halogen ion, it is desirable. The etch residue 25 as shown in drawing 7 is effectively removable with such processing.

[0045] If etch residues, such as a resultant in the case of etching, are flooded with the solution with which superfluous halogen ion exists, a dissolution balance will collapse, and this is considered for an etch residue to dissolve into the solution of an alkali-halide metal salt promptly. Moreover, if immersed in the solution of a sodium thiosulfate, it will be considered for etch residues, such as a silver halide, to dissolve promptly.

[0046] As acid solution containing halogen ion, HCl, HBr, HI, ferric-chloride solution, etc. are mentioned, and NaCl, KCl, NaBr, etc. are mentioned as an alkali-halide metal salt. It is desirable to consider as a 0.5M not less in respect of positive removal of an etch residue as concentration of an alkali-halide metal salt. Moreover, as concentration of a sodium thiosulfate, 0.1-3M are desirable.

[0047] As the second patterning method in this invention, as shown in drawing 8, on a base, a desired pattern is formed in an alkali solution or an organic solvent using a melttable resist, subsequently the aforementioned transparent electric conduction film is formed, and the method of exfoliating the unnecessary portion of this transparent electric conduction film the whole resist by the alkali solution or the organic solvent is mentioned after that.

[0048] What melted the novolak resin which contained a photosensitive material in the alkali solution or the organic solvent as a melttable resist 26 to organic solvents, such as ethylene-glycol-monoethyl-ether monochrome acetate, is mentioned. The alkali solution which contained NaOH 0.5 to 3% of the weight to the solution as an alkali solution of exfoliation liquid, the alkali solution which contained hydroxylation tetramethylammonium two to 3% of the weight to the solution, or the organic alkali solution which consists of o-dichlorobenzene, a phenol, and an alkylbenzene sulfonic acid is mentioned.

[0049] As an organic solvent of ablation liquid, organic solvents, such as an isopropanol, dimethyl sulfoxide, ethylene glycol, and a trichloroethylene, are mentioned. If a resist and ablation liquid give a damage to neither a transparent electric conduction film nor a base, they will not be limited especially. As the membrane formation method of the transparent electric conduction film after resist pattern formation, in order to avoid the thermal damage to a resist, it is desirable to form membranes at the substrate temperature of 150 degrees C or less.

[0050] In case it is that the arbitrary electrode patterns after membrane formation can be formed as a feature of the first above-mentioned patterning method, and membrane formation, it is mentioned that there is no film property degradation by degasifying from a resist. On the other hand, the etching-reagent composition with the second complicated patterning method and optimization of etching conditions have the feature that there are also few etch residues, such as a resultant with being unnecessary and an acid, and a high patterning precision and a good pattern configuration are acquired.

[0051] The transparent electric conduction film and the transparent-electrode formation method of this invention are applicable also to TFT (TFT) type LCD as shown in drawing 9. drawing 9 — setting — 27 — a gate electrode and 28 — for a pixel electrode and 31, as for a source electrode and 33, a drain electrode and 32 are [a gate insulator layer and 29 / a semiconductor layer and 30 / a pixel electrode unification drain electrode and 34] source electrodes

[0052] This invention offers the substrate with electrode wiring for LCD in which the source electrode, drain electrode, and pixel electrode of TFT type LCD were formed by the aforementioned transparent electric conduction film. After this invention forms a gate electrode, a gate insulator layer, and a semiconductor layer on a base, it forms the aforementioned transparent electric conduction film, and offers the formation method of the substrate with electrode wiring for LCD characterized by forming the drain electrode which subsequently united this transparent electric conduction film with the source electrode and the pixel electrode by carrying out etching processing again.

[0053] By using the aforementioned transparent electric conduction film as the source electrode 32, the drain electrode 31, and a pixel electrode 30, package membrane formation of the source, a drain, and a pixel electrode and package patterning become possible, and the effect excellent in the improvement in productivity or reduction of a defect is demonstrated.

[0054]

[Example] The transparent electric conduction film of composition as shown in Examples 1-18 (all are the examples) and Examples 19-20 (all are the examples of comparison) of Tables 1-2 was formed by DC sputtering on the base 1 which formed beforehand the acrylic transparent resin protective layer 8 for the glass substrate 39 as shown in drawing 2, the light-filter layer 7, and protection of a light filter and smoothing, and the non-in-a-plane intermediate layer 9 which consists of a silica film.

[0055] In ZnO When forming the film made into a principal component, membranes were formed using the In₂O₃ sintered-compact ("In₂O₃ 10 atom % containing Sn" is called "ITO" below) target 10 atom % Containing Sn in the atmosphere of Ar gas 3mTorr containing 3 volume % oxygen. When forming the film which makes ZnO a principal component, membranes were formed in the atmosphere of Ar gas 3mTorr using the ZnO ("ZnO pentatomic % containing Ga" is called "GZO" below) sintered-compact target pentatomic % Containing Ga.

[0056] When an oxide layer was considered as multilayer composition, the laminating was carried out to the portion which carries out the laminating of an ITO layer and the GZO layer by turns, and touches Ag layer at the topmost part of the best layer oxide layer so that an ITO layer might be arranged so that a GZO layer might be arranged.

[0057] When forming a mixed oxide, the atomic ratio of In and Zn formed membranes using the sintered-compact target of various mixed oxides used as 4:6 (a table describes mixture 1), 8:2 (a table describes mixture 2), and 9:1 (a table describes mixture 3) in the atmosphere of Ar gas 3mTorr containing 3 volume % oxygen. moreover, the multilayer of front Naka — 1 — the thickness of ITO — the thickness of about 3nm and GZO — about 7nm — carrying out — a multilayer — 2 set thickness of about 7nm and GZO to about 3nm for the thickness of ITO and a multilayer — 1 and a multilayer — 2 — between an A base and metal layers — base/ITO/GZO... between /ITO/GZO / metal layer, an I metal layer, and metal layers — metal layer /GZO/ITO... on /ITO/GZO / metal layer, and the metal layer besides U **, the laminating was carried out by turns so that it might become a metal layer / GZO/ITO...GZO/ITO

[0058] The metal layer formed membranes in the atmosphere of Ar gas 3mTorr using the various targets of Pd, Au, Ag, Ag alloy (1%PdAg) containing Pd of 1 atom %, or Ag alloy (1%AuAg) containing Au of 1 atom %. Sputtering power and membrane formation time adjusted the thickness of each film. Pd rich layer and Ag rich layer of front Naka changed the sputtering power of each target, and they were produced so that Pd rich layer thickness might be set to about 1nm so that sputtering of Pd target and the Ag target might be carried out simultaneously. Pd composition ratio might become high by the interface with an oxide layer (50% or more) and Ag composition ratio might become high in the core of a metal membrane (50% or more).

[0059] Moreover, after membrane formation, the case where heat treatment for [250 degree-Cx] 30 minutes was performed was considered as heat treatment "****" in the atmosphere, and it was shown in the table, having used as "nothing" the case where it did not carry out. Moreover, the number in () of front Naka is thickness (nm).

[0060] About the sample shown in Examples 1-20 of Table 1 and Table 2, one resistance, 2 visible light transmittance, 3 patterning nature, 4 moisture resistance, and 5 alkali resistance were evaluated. In addition, the evaluation method 3 patterning

nature, 4 damp-proof, and 5 alkali-proof is shown in Table 3.

[0061] After patterning applied the resist and formed the resist pattern of the shape of a stripe with a line width of face [of 130 micrometers], and a space width of face of 20 micrometers by the photolithography method on each transparent electric conduction film shown in Table 1 and Table 2, the etching reagent shown below performed it. Namely, about Examples 4, 6, and 19, the etching reagent of the ferric chloride which served both as acid solution and the oxidizer is used. About each, it carries out, after determining the concentration optimal from the range whose hydrogen ion concentration is 0.01~6M, about the other example Using the etching reagent which consists of a hydrochloric acid (acid solution) and a ferric chloride (oxidizer), about each, hydrogen ion concentration carried out, after determining the optimal composition concentration from the range 0.1~5M, and whose oxidizer concentration are 0.01~1.5M. A result is as being shown in Tables 1 and 2.

[0062] Next, in order to investigate the effective composition range of an etching reagent in detail, patterning of the transparent electric conduction film was carried out using the etching reagent of various composition. That is, after forming a resist pattern like the above on the transparent electric conduction film of Example 1, patterning nature was evaluated using the etching reagent of the various composition shown in Table 4. A result is as being shown in Table 4. When Examples 2~18 were followed in the same patterning nature evaluation by the etching reagent of various composition, the same result as the case of Example 1 was obtained. Furthermore, about Example 4, it carried out using the etching reagent of the various concentration shown in Table 5. A result is as being shown in Table 5. When Examples 6 and 19 were followed in the same patterning nature evaluation by the etching reagent of various composition, the same result as the case of Example 4 was obtained. On the other hand, although patterning was tried about Example 20 by the etching reagent of the various composition shown in Tables 4 and 5, patterning nature good in any case was not obtained.

[0063] In addition, the concentration in Table 5 shows hydrogen ion concentration, moreover, O shown in Table 4 and Table 5 — the amount of side etching — 4 micrometers or less and O — the amount of side etching — 4 micrometers — super — as for 5 micrometers or less and x, the amount of side etching means 5-micrometer **

[0064] As shown in Table 4 and Table 5, in the field of low concentration, an etch rate falls and the amount of side etching also increases composition of etchant from the optimal acid concentration. In the field of concentration higher than the optimal acid concentration, an etch rate becomes quicker than required and the amount of side etching also becomes large. About the oxidizer, the inclination which the dissolution of Ag layer cannot progress easily, the amount of side etching also increases in the field of low concentration, and the amount of side etching increases from the optimal oxidizer concentration also in the field of concentration higher than the optimal oxidizer concentration was suited.

[0065] the acid solution which contained the ferric chloride especially — using — etching — it was immersed in the solution of the alkali-halide metal salt of 5M the back the bottom — a thing — when the thing compared the removal effect of an etch residue, the result with what [good] was immersed in the solution of an alkali-halide metal salt was obtained Moreover, similarly, it replaced with the solution of the above-mentioned alkali-halide metal salt after etching, and when immersed in the solution of the sodium thiosulfate of 1M, the good result was obtained.

[0066] Many performances of the transparent electric conduction film of this invention are shown in Tables 1 and 2. In 3 layer membrane composition of the transparent oxide and Ag layer which are shown in Examples 1~14 and Examples 19~20, resistance 3~4ohm/**, and the transparent electric conduction film of 74 ~ 76% of visible light transmittances were obtained, and 2ohms of resistance, ** grade, and the transparent electric conduction film of about 73% of visible light transmittances were obtained in 5 layer membrane composition shown in Examples 15~18. Moreover, **** of a visible light transmittance and low resistance-ization were able to be attained also with heat treatment after membrane formation.

[0067] In the case where the transparent electric conduction film shown in Examples 1~19 is used, it has a sharp pattern edge configuration, and most etch residues were not seen, but patterning nature also with the as good amount of side etching as about 2~4 micrometers was obtained. Also about moisture resistance, generating of the luminescent spot (fault) with a diameter of 0.5mm or more was not seen, but the good performance was obtained.

[0068] In 2O3 shown in Example 19 The alkali resistance of the composition using the oxide film which is not included is not necessarily enough. Alkali resistance is In 2O3 to ZnO. It improves, so that a mixing ratio increases, or, so that the ratio of the thickness of an ITO layer to a GZO layer increases. However, In 2O3 If a component ratio exceeds 98 atom %, or if the ratio of the thickness of an ITO layer exceeds 95%, patterning nature and moisture resistance will fall.

[0069] As shown in Examples 7, 8, 14, 16, 17, and 18, it is In 2O3 about the topmost part of the best oxide layer. By considering as a layer with many components, the attack of the alkali from a film front face can be prevented effectively. However, if this thickness exceeds 50nm, patterning nature will fall.

[0070] As shown in Examples 11~15, improvement in a visible light transmittance and low resistance-ization can be attained by considering a metal layer as multilayer composition or inclination composition composition. On the other hand, by the film which has the composition which sandwiched the film which makes a principal component Ag shown in Example 20 by the ITO film, although excelled in alkali resistance, ablation by the interface of a metal membrane and an ITO film was intense, a desired electrode pattern was not obtained, and much luminescent spots (fault) with a diameter of 1mm or more occurred also about the damp-proof test, and the good result was not obtained.

[0071] Next, on the base 1 by which the acrylic transparent resin protective layer 8 for the light-filter layer 7, and protection of a light filter and smoothing and the non-in-a-plane intermediate layer 9 which consists of a silica were beforehand formed on the glass substrate 39 as the second patterning method The photoresist which consists of a novolak system resin is applied. by the usual photolithography method Line width of face of 130 micrometers, After forming the stripe-like pattern 26 used as space width of face of 20 micrometers (drawing 8 (a)), the transparent electric conduction film of composition of being shown in Examples 1~18 was formed by DC sputtering. Substrate heating was not performed (drawing 8 (b)). Then, adding supersonic oscillation, by the solution of NaOH, the unnecessary portion of a transparent electric conduction film was exfoliated the whole resist, and the desired electrode pattern was formed (drawing 8 (c)).

[0072] Consequently, no residue of a transparent electric conduction film was looked at by the space section also about which case, but the edge configuration was also very sharp and, moreover, what also has as good the dimensional accuracy of pattern width of face as about 1~2 micrometers was obtained.

[0073] Moreover, the transparent electric conduction film of composition of being shown in Examples 1~18 was formed by DC sputtering on the glass substrate, without performing substrate heating. About some films, 250 degrees C and heat treatment for 30 minutes were performed in the atmosphere after membrane formation. Then, the resist was applied and the resist pattern which imitated the source 34 for TFT type LCD as shown in drawing 9 (b), the drain 33, and the pixel electrode (InSn_xO_y) 33 was formed.

[0074] Furthermore, electrode pattern formation was tried using HI (hydrogen iodide) and Ar gas using the dry etching system as shown in drawing 10. Consequently, the pattern edge configuration was sharp, the etch residue etc. was not seen but the result with which it can be satisfied of the amount of side etching as about 1–2 micrometers, the source for TFT type LCD, a drain, and a pixel electrode was obtained. In drawing 10, in RF power supply and 36, a cathode electrode and 37 show a sample and 38 shows [35] an anode electrode.

[0075]

[Table 1]

	層構成	熱処理	抵抗 Ω/□	可視光 透過率 %	バターニン ガ	耐湿性 40 ℃、 90%RH、 1週間	耐塩水 性
	混合 1 : In と Zn の原子比が 4 : 6 の混合物 混合 2 : In と Zn の原子比が 8 : 2 の混合物 混合 3 : In と Zn の原子比が 9 : 1 の混合物 多層 1 : ITO(3nm) と CZO(7nm) の多層構成 多層 2 : ITO(7nm) と CZO(3nm) の多層構成						
例 1	基体 / 混合 2 / 1%PdAg / 混合 2 (16) / (11) / (38)	無し	3. 6	74.3	○	○	B
例 2	基体 / 多層 2 / 1%PdAg / 多層 2 (16) / (11) / (38)	無し	3. 5	74.5	○	○	B
例 3	基体 / 混合 2 / 1%PdAg / 混合 2 (16) / (11) / (38)	有り	3. 0	75.4	○	○	B
例 4	基体 / 混合 1 / 1%PdAg / 混合 1 (16) / (11) / (38)	有り	3. 1	75.3	○	○	C
例 5	基体 / 多層 2 / 1%PdAg / 多層 2 (16) / (11) / (38)	有り	2. 9	75.2	○	○	B
例 6	基体 / 多層 1 / 1%PdAg / 多層 1 (16) / (11) / (38)	有り	3. 0	75.2	○	○	C
例 7	基体 / 混合 2 / 1%PdAg / 混合 2 / 混合 3 (16) / (11) / (18) / (20)	有り	3. 1	75.3	○	○	A
例 8	基体 / 多層 2 / 1%PdAg / 多層 2 / ITO (16) / (11) / (18) / (20)	有り	3. 0	75.1	○	○	A
例 9	基体 / 混合 3 / 混合 2 / 1%PdAg / 混合 2 (6) / (10) / (11) / (38)	有り	3. 1	75.3	○	○	B

[0076]

[Table 2]

例 10	基体 / ITO / 多層 2 / 1%PdAg / 多層 2 (6) / (10) / (11) / (38)	有り	3. 1	75.2	○	○	B
例 11	基体 / 混合 2 / Pd / Ag / Pd / 混合 2 (16)/(0.5)/(10)/(0.5)/(38)	有り	2. 8	75.7	○	○	B
例 12	基体 / 混合 2 / Pd / Ag / Pd / Ag / Pd / 混合 2 (16)/(0.5)/(5)/(0.5)/(5)/(0.5)/(38)	有り	2. 9	75.5	○	○	B
例 13	基体 / 混合 2 / Au / Ag / Au / Ag / Au / 混合 2 (18)/(0.5)/(5)/(0.5)/(5)/(0.5)/(38)	有り	2. 7	75.8	○	○	B
例 14	基体 / 混合 2 / Pd _{1-x} Ag _x / Pd _{1-x} Ag _x / 混合 2 / 混合 3 (40) / (1) / (9) / (1) / (20) / (20) Pd _{1-x} Ag _x :Pd(5)%以上の層、Ag _{1-x} Pd(5)%以上の層	有り	2. 9	75.5	○	○	A
例 15	基体 / 混合 2 / Pd / Ag / Pd / 混合 2 / Pd / Ag / Pd / 混合 2 (40)/(0.5)/(10)/(0.5)/(90)/(0.5)/(10)/(0.5)/(40)	有り	1. 9	73.8	○	○	B
例 16	基体 / 混合 2 / 1%PdAg / 混合 2 / 1%PdAg / 混合 2 / ITO (40) / (11) / (90) / (11) / (20) / (20)	有り	2. 1	73.3	○	○	A
例 17	基体 / 混合 2 / 1%AuAg / 混合 2 / 1%AuAg / 混合 2 / 混合 3 (40) / (11) / (90) / (11) / (20) / (20)	有り	1. 9	74.0	○	○	A
例 18	基体 / 多層 2 / 1%PdAg / 多層 2 / 1%PdAg / 多層 2 / ITO (40) / (11) / (90) / (11) / (40) / (20)	有り	2. 0	73.5	○	○	A
例 19	基体 / CZO / 1%PdAg / CZO (16) / (11) / (38)	有り	3. 0	75.4	○	○	D
例 20	基体 / ITO / 1%PdAg / ITO (16) / (11) / (38)	有り	3. 6	76.0	×	×	A

[0077]

[Table 3]

耐アルカリ性の判定	1 wt%NaOH 室温、10分	1 wt%NaOH 室温、20分	3 wt%NaOH 室温、20分	3 wt%NaOH 60°C、20分
A	OK	OK	OK	OK
B	OK	OK	OK	NG
C	OK	OK	NG	NG
D	OK	NG	NG	NG
バーニング性の判定			耐湿性の判定	
○：サイドエッチ2~4 μm程度 パターン形状良好、残渣なし		○：0.5 mm以上の欠点なし		
×：サイドエッチ10 μm以上 パターン剥離発生		×：1 mm以上の欠点発生		

[0078]

[Table 4]

酸化剤	塩 鹽 (室温)					
	0. 01M未満	0. 01~0. 1M	0. 1~5M	5~6M	6M超過	
塩化第二鉄	0.0001M 未満	×	×	×	×	
	0.0001M から 0. 01M	×	○	○	×	
	0. 01M から 1. 5M	×	○	○	×	
	1. 5M 超過	×	○	○	×	
酸	臭化水素酸 (室温)					
	0. 01M未満	0. 01~3M	3~9M	9M超過	工業的なHB入手できず、 実施困難と判断した。	
	0.0001M 未満	×	×	×		
	0.0001M から 0.0005M	×	○	○		
	0. 0005M から 0. 5M	×	○	○		
	0. 5M 超過	×	○	○		

[0079]

[Table 5]

塩化第二鉄 (室温)		
0. 01M未満	0. 01~6M	6M超過
×	○ エッジ進まず	×

[0080]

[Effect of the Invention] According to this invention, the transparent electric conduction film which the low specific resistance [thickness / sum total / of a transparent electric conduction film] below the sheet resistance of 3ohms / ** can be realized easily, and is moreover excellent in 300nm or less at endurance, such as alkali resistance and moisture resistance, can be offered.

[0081] Moreover, according to the electrode formation method of this invention, it is cheap and an accurate electrode can be processed.

[0082] In addition to on glass, since the transparent electric conduction film of this invention can be formed also on the low (100 degrees C or less) plastics of membrane formation temperature, and the substrate with a light filter for colors LCD (250 degrees C or less), it is the optimal as a transparent-electrode film for electronic displays which needs low resistance of electroluminescence displays including LCD, a plasma display, or an electrochromic element, and can be offered by the low cost as compared with the former. Especially, in simple matrix type LCD, the effect excellent in display upgrade, such as enlargement of a screen product and cross talk reduction, is demonstrated.

[0083] Moreover, also in TFT type LCD, by using as a source electrode, a drain electrode, and a pixel electrode, package membrane formation of the source, a drain, and a pixel electrode and package patterning become possible, and the effect excellent in the improvement in productivity or reduction of a defect is demonstrated.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] (a) The cross section of an example of the three-layer membrane system transparent electric conduction film of this invention, the cross section of an example of the five-layer membrane system transparent electric conduction film of the (b) this invention.

[Drawing 2] The cross section of the substrate for color LCD used for this invention.

[Drawing 3] The cross section of an example of the transparent electric conduction film whose oxide layer of this invention is multilayer structure.

[Drawing 4] (a) The best transparent oxide layer of this invention is In₂O₃. It is the layer which consists of a multilayer of the film made into a principal component, and the film which makes ZnO a principal component. The film which tends to keep away from a base is In₂O₃. The cross section of an example of the transparent electric conduction film which consists of a multilayer which piled up the film so that a content might increase, (b) The best transparent oxide layer of this invention is In₂O₃. It is a mixed-oxide layer with ZnO. It is In₂O₃ to the direction of thickness as it goes in a base and the direction keeping away. The cross section of an example of the transparent electric conduction film which consists of a layer which has the inclination composition which a content increases, (c) The transparent oxide layer near the base of this invention is In₂O₃. It is the layer which consists of a multilayer of the film made into a principal component, and the film which makes ZnO a principal component. The film which tends to approach a base is In₂O₃. The cross section of an example of the transparent electric conduction film which consists of a multilayer which piled up the film so that a content might increase, (d) The transparent oxide layer near the base of this invention is In₂O₃. It is In₂O₃ to the direction of thickness as it is a mixed-oxide layer with ZnO and goes in the direction approaching a base. Cross section of an example of the transparent electric conduction film which consists of a layer which has the inclination composition which a content increases.

[Drawing 5] (a) The cross section of an example of the transparent electric conduction film with which it is placed between the interfaces of the metal layer containing Ag which is this invention, and an oxide layer by other metals other than Ag, the cross section of an example of the transparent electric conduction film which used the inclination composition metal membrane with other high metal composition ratios other than Ag for the interface of the metal layer containing Ag of the (b) this invention, and an oxide layer.

[Drawing 6] (a) The cross section of an example of the transparent electric conduction film whose metal layer of this invention is multilayer structure, the cross section of an example of the transparent electric conduction film whose metal layer of the (b) this invention is the inclination composition metal membrane of metals other than Ag and Ag.

[Drawing 7] The ** type view showing signs that the etch residue arose.

[Drawing 8] The ** type view showing the patterning method of this invention.

[Drawing 9] (a) The ** type view of the electrode wiring for TFT type LCD in connection with the operation gestalt of the ** type view of electrode wiring and the (b) this invention for TFT type LCD in connection with the conventional example.

[Drawing 10] The ** type view of the dry etching system used in an example.

[Description of Notations]

- 1: Base,
- 2, 4, 6: Transparent oxide layer,
- 3: the metal layer containing 5:Ag,
- 7: Light-filter layer,
- 8: Transparent resin protective layer,
- 9: Non-in-a-plane intermediate layer,
- 10: In₂O₃ Film made into a principal component,
- 11: The film which makes ZnO a principal component,
- 12: A film with few contents of In than 13,
- 13: A film with more contents of In than 12,
- 14: The content of In is the portion of under 50 atom %.
- 15, 17, other metal layers other than 21:Ag,
- 16: the metal layer containing 22:Ag,

Other metal composition ratios other than 18, 20, 23, and 24:Ag are 50% or more of metal layers.

19: The composition ratio of Ag is 50% or more of metal layer.

25: Etch residue,

26: Resist,

27: Gate electrode,

28: Gate insulator layer,

29: Semiconductor layer,

30: Pixel electrode,

31: Drain electrode,

32: Source electrode,

33: Pixel electrode unification drain electrode,

34: Source electrode,

- 35: RF power supply,
- 36: Cathode electrode,
- 37: Sample,
- 38: Anode electrode,
- 39: Glass substrate,
- 40: The content of In is a portion more than 50 atom %.

[Translation done.]

* NOTICES *

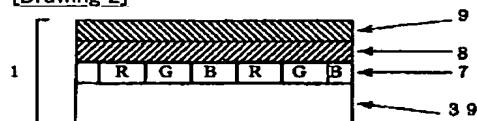
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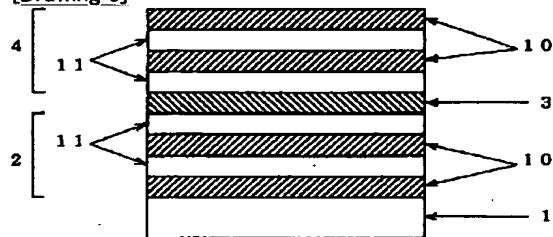
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DRAWINGS

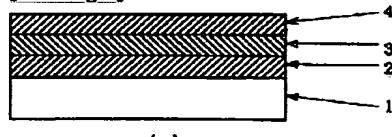
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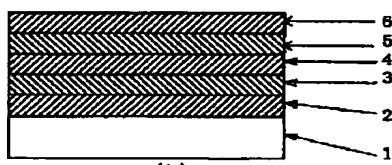
[Drawing 3]



[Drawing 1]



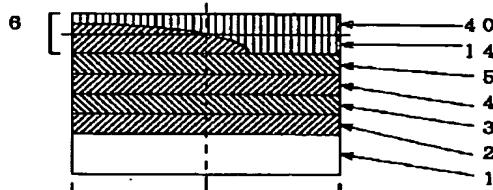
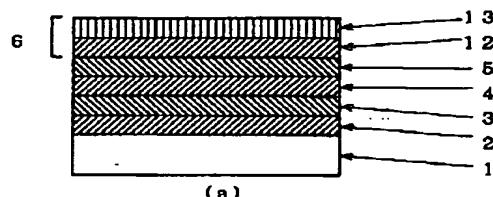
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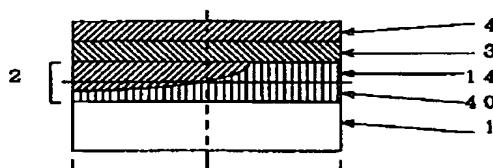
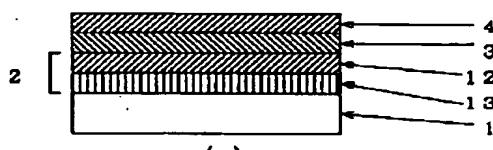
(b)

[Drawing 4]

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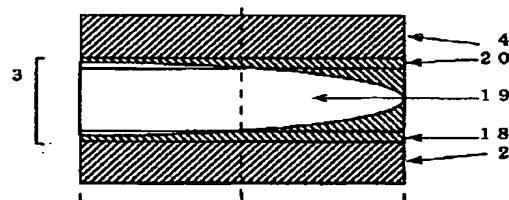
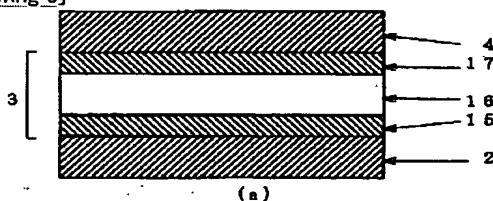


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In 比率 100 50 0

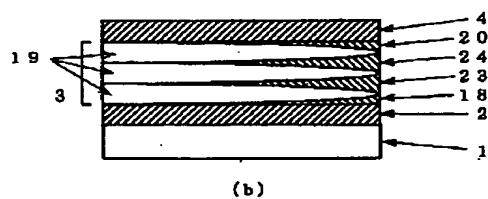
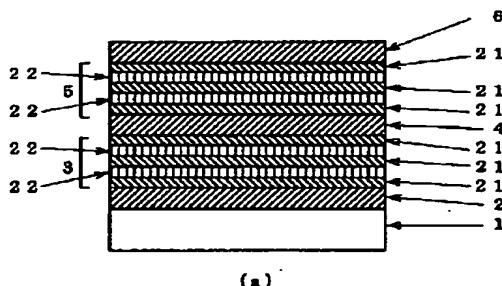
[Drawing 5]



Ag 比率 : 0 50 100%
他金属比率 : 100 50 0 %

[Drawing 6]

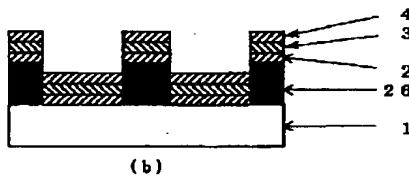
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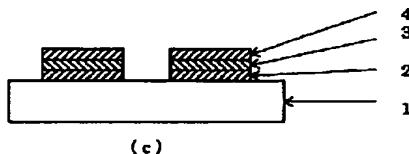
[Drawing 8]



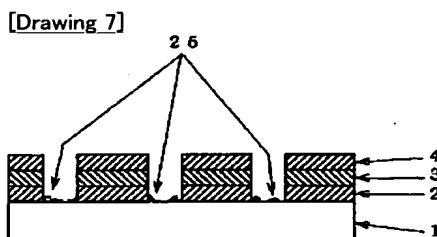
(a)



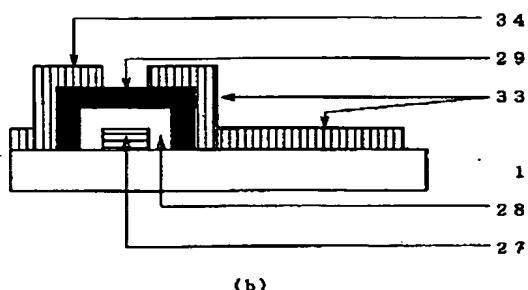
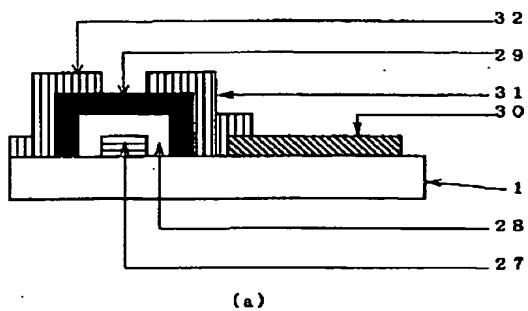
(b)



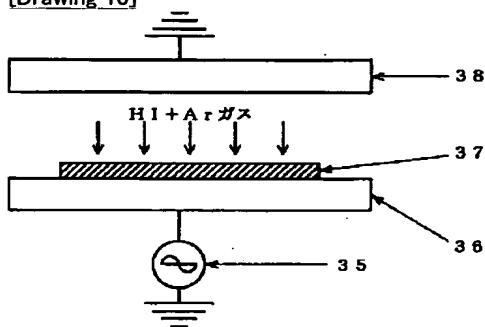
(c)



[Drawing 9]



[Drawing 10]



[Translation done.]